

ON LOCAL HIGH ELECTRIC FIELD-INDUCED MODIFICATIONS OF A NIOBIUM OXIDE SURFACE

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Abstract

A (110) surface of a niobium crystal prepared in UHV has been studied by Auger Electron Spectroscopy (AES) and Scanning Tunneling Microscopy (STM). This surface is covered, after annealing, by a thin overlayer of $\text{NbO}_{x \approx 1}$, due to surface segregation of O dissolved in the bulk. This niobium oxide layer exhibits a complex surface structure, which is stable and reproducible, consisting of a defective arrangement of parallel sticks (length ≈ 3 nm, width ≈ 0.6 nm). First results on permanent and irreversible modifications of $\text{NbO}_{x \approx 1}$ surface, induced by applying a bias voltage between a STM W-tip and the sample higher than a voltage threshold $|V_t^{\text{mt}}| \approx 2.5$ V, are presented. The origin of bias voltage-induced degradations is discussed. Finally, the involved electric field and the critical peak field which limits accelerating performances of RF cavities are compared.

1 INTRODUCTION

One of the main limitations of superconducting radio frequency (SCRF) cavities [1] for particle accelerators is field emission of electrons from the niobium surface in the presence of high electric fields. Electron field emission (EFE) [2] [3] can absorb a significant portion of the available RF power as well as produce unwanted beam and X-ray radiation. Furthermore, it may induce voltage breakdowns which rapidly limit the field gradient. Important progress have been made in the understanding of its mechanisms and in treatments to cure it [4]. Micrometer-scale studies have shown that the limitation is essentially due to field enhancement from contaminants and / or defects present on the surface. The protrusion on protrusion model [5] accounts for it, but, at a nanometer-scale, validation of this model remains yet to be proved. Furthermore, definite physical meanings of the parameters β (geometrical field enhancement factor of an emitter) and S (effective emitting area) associated to the Fowler-Nordheim theory [6] [7] are still missing at nanometer-scale.

Besides, the different niobium oxides which cover any RF cavity surfaces have been the object of extensive studies [8] - [14]. Oxide growth and coatings on niobium have been mainly studied by XPS and AES for different surface preparations. Two oxides are important on Nb surfaces: a thin (≤ 1 nm) metallic oxide $\text{NbO}_{x \approx 1}$ and a

thick and porous dielectric oxide Nb_2O_5 overlayers [8] - [10]. Concerning the fine surface structure of these oxides and its behavior under a high electric field, none specific studies have been done until now.

In this paper, evidence of modifications of the thin niobium oxide layer induced by a local application of a high electric field is reported. We have used a STM [15] as a tool to explore the surface structure of this oxide as well as to apply local high electric field (several GV.m^{-1}) on the surface with the STM tip.

2 EXPERIMENTAL

All the experiments were performed in an UHV chamber with a base pressure of 5×10^{-11} Pa with facilities for transferring samples and STM tips. The main chamber is equipped with a commercial STM (Omicron1) and a Cylindrical Mirror Analyzer for in situ Auger electron spectroscopy (AES).

Samples (discs of $\varnothing 6$ mm and 2 mm thick) which were cut in a single crystal of Nb (purchased from Goodfellow) were chemically polished in a standard acid mixture (HF (25 % vol.), HNO_3 (25 % vol.) and H_3PO_4 (50 % vol.)) prior to mounting on a sample holder. The sample Residual Resistivity Ratio (RRR) is 30, corresponding to an overall impurity concentration of about 500 ppm. The surface orientation was checked by X-ray diffraction. In vacuum, the samples suffer many cycles of Ar^+ -sputtering (1keV) and annealing between 1000 K and 2300 K (typical duration 30-60 minutes). After sputtering, AES spectra of the surface display only Nb peaks (Fig. 1(a)). After annealing, one main extra peak appears at 520 eV which is identified with the O Auger transition. Another weak peak is attributed to carbon due to bulk contamination (Fig. 1(b)). This oxygen is due to surface segregation of O atoms diluted in the Nb bulk (during the annealing treatment). The ratio of the measured height of O and Nb AES-peaks is equal to 0.4, after an annealing at 2200 K. As such a value was attributed to the presence of a thin NbO film [8], we conclude that the surface is covered by a thin $\text{NbO}_{x \approx 1}$ overlayer.

STM measurements were performed in constant-current mode at room temperature. STM is a technique allowing direct imaging of solid surfaces with unprecedented resolution. The operation of a STM is based on the so-called tunneling current, I_t , which starts to flow when a

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sharp tip approaches a conducting surface at a distance of approximately one nanometer, a voltage, V_t , being applied between the tip and the sample. The tip is mounted on a piezoelectric tripod, which allows tiny movements by applying a voltage at its electrodes. Thereby, the electronics of the STM system control the tip position in such a way that I_t is kept constant (therefore the tip-surface distance, d , too), while, at the same time scanning a small area of the sample surface. This Z-movement of the tip is recorded and can be displayed as an image of the surface topography. Under ideal circumstances, the individual atoms of a surface can be resolved and displayed. A STM image of a surface is a view of its electronic structure near the Fermi energy level. Therefore, it mixes electronic and geometrical data from which chemical information are difficult to extract.

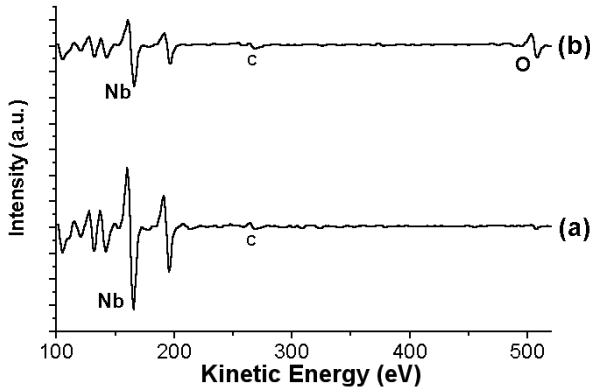


Figure 1: Auger spectra of the Nb(110) surface. (a) After Ar^+ -sputtering (900 eV during 1h). (b) After annealing in UHV (2000K during 30 min.).

STM tips were electrochemically etched from a W wire (\varnothing 0.25 mm) in a 2 M solution of KOH. In vacuum, these tips are cleaned by electron heating and ion sputtering.

3 RESULTS AND DISCUSSION

3.1 STM images of $\text{NbO}_{x \approx 1}$ surface structure

After annealing at T varying in a large range (1000K to 2500K), the sample surface displays a complex and reproducible structure. Fig. 2(a) shows a typical STM image of this structure for an overlayer of $\text{NbO}_{x \approx 1}$ covering the Nb(110) surface. This oxide surface structure can be described as a defective arrangement of parallel sticks 28 Å long, having a small dispersion of 2 Å. In contrast, one notices variations in the lateral distance that separate two neighboring sticks. Fig. 2(b) reveals that, at high resolution, the atomic structure of this layer is very complex. This poor-ordered structure is probably related to local changes in the oxide stoichiometry (oxygen vacancies). A detailed study of this structure will be published elsewhere.

Local deviations of the sample surface from the Nb(110) plane induce the formation of steps, as shown in Fig. 3 and Fig. 4. Their density and mean orientation depend on the surface miscut.

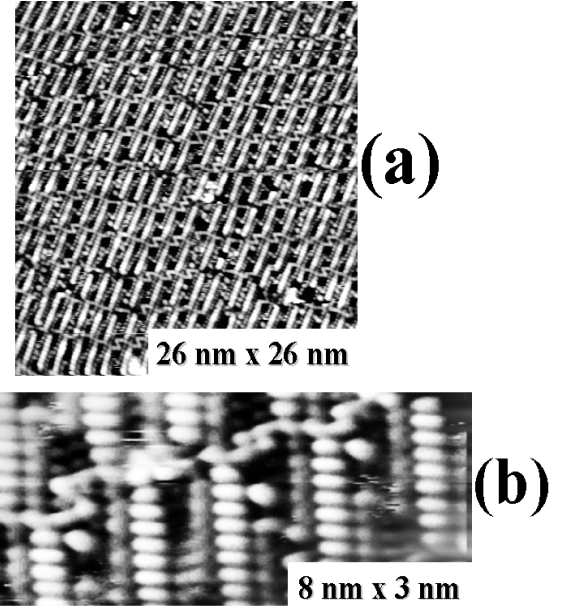


Figure 2: STM image showing the $\text{NbO}_{x \approx 1}$ surface structure. (a) Imperfect arrangement of parallel sticks. (b) High resolution image showing several atomic defects.

3.2 Permanent $\text{NbO}_{x \approx 1}$ surface modifications induced by increasing $|V_t|$

In this work, we use the STM as a tool for imaging surface structure of $\text{NbO}_{x \approx 1}$, but also to investigate the influence of a local high electric field on the niobium oxide. This was done by applying a high bias on the tip. In order to show the behavior of this oxide under high electric fields, we have proceeded in three steps: first, a STM image of the $\text{NbO}_{x \approx 1}$ surface structure is taken as reference with standard tunneling conditions (V_t ranges from 0.1 V to 1 V in each polarity). In the second step, a small area of the last image is scanned raising V_t to a modifying voltage V_t^m . Typically, V_t^m ranges from - 10 V to + 10 V such as $|V_t^m| \geq 1$ V. The STM feedback loop is always active during this process, maintaining the tip-surface distance constant. In the last step, the scanned area is back to the reference one and a new image with standard tunneling conditions is performed. In that way, comparison between the latest image and the first one reveals any differences due to the high electric field applied to tip in step two.

Here only some typical results are presented. In Fig. 3(a), STM images of the $\text{NbO}_{x \approx 1}$ surface structure show a high density of steps appearing as vertical lines. The scanned area, with a tip voltage at - 4.2 V (Fig. 3(b)) and + 4.2V (not shown here), appears clearly in the white

square. This modified area is covered with white spots but steps are still visible inside. Furthermore, similar surface modifications are caused by a different tip at +4.5 V (Fig. 3(c) and Fig. 3(d)) and -4.5 V (not shown here). So, these tip-induced modifications do not depend on the polarity of the bias applied. They are also not very sensitive to the shape of the W-tip apex. These surface modifications seem to be irreversible and permanent as they have been observed lasting even several hours later. As clearly shown in Fig. 4, there exists a bias voltage threshold V_t^{mT} at which the surface modification starts. It is also independent on the bias voltage polarity (not shown here). In that series of STM images, the left side of each image gives the surface morphology after a tip scanning with different positive values of V_t^m . The right side is taken as reference. Voltage modifications take place for an applied bias $1.8 \text{ V} \leq V_t^{mT} \leq 2.8 \text{ V}$. In fact, five different W-tips and several $\text{NbO}_{x \approx 1}$ surfaces have been studied and the average threshold is found to be $V_t^{mT} = 2.5 \pm 0.5 \text{ V}$. Obviously, to reduce this dispersion, a larger number of investigations are required.

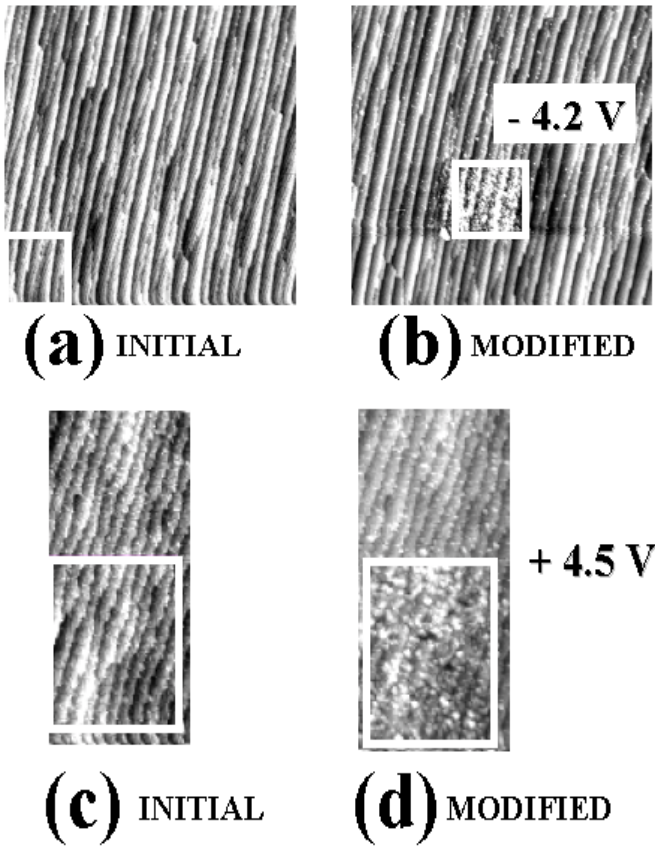


Figure 3: Four STM images ((a) and (b) 200 nm x 200 nm, (c) and (d) 43 nm x 100 nm) showing the permanent modifications of the $\text{NbO}_{x \approx 1}$ stepped surface structure. (a) and (c) Scanned area (white frame) before increasing of the absolute value of the bias voltage. (b) The same scanned area (white frame) than in (a) after applying a negative bias voltage - 4.2 V on the W-tip. (d) The same scanned area (white frame) than in (c) after applying a

positive bias voltage of + 4.5 V on the W-tip. For (a) and (b), we have used a W-tip and for (c) and (d), another W-tip was used.

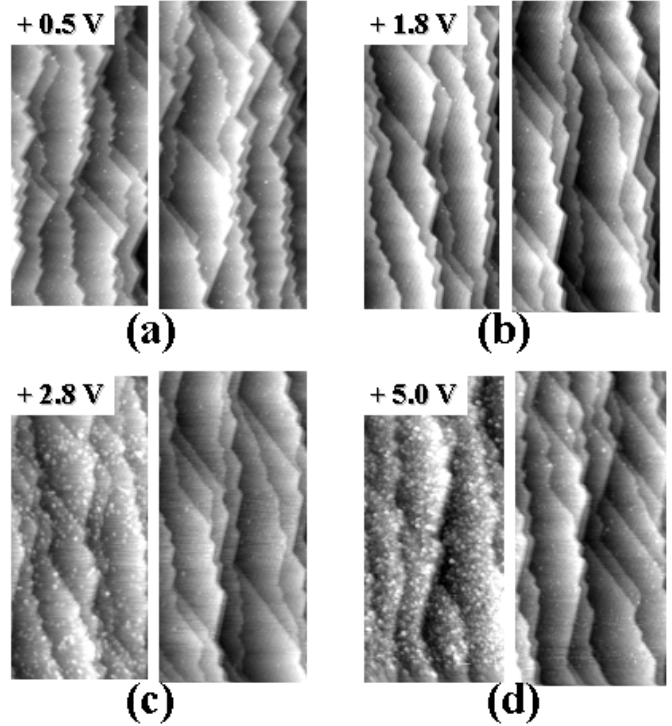


Figure 4: Four STM images (150 nm x 150 nm) showing the existence of a positive bias voltage threshold and the increasing of white spot density on the $\text{NbO}_{x \approx 1}$ stepped surface structure with the increase of positive bias voltage. The left side of each image corresponds to the “perturbed” area and the right one is taken as reference. White spots appear between + 1.8 V and + 2.8 V. The study for negative bias voltages shows the same characteristics as positive bias voltages and white spots appear between -1.8 V and -2.8 V (not shown here).

These images raise the following question: what is the true nature of these modifications induced by high bias voltages applied on the tip? In order to bring some elements of answer, a $\text{NbO}_{x \approx 1}$ surface was scanned with a tip at 2.5 V, near V_t^{mT} . Fig. 5 presents the results obtained. In the right part of this image, where the high voltage has been applied, the area exhibits unperturbed step edges where some sticks have been modified, some vanished and several white spots emerged. The left part is taken as reference. So, atoms of the $\text{NbO}_{x \approx 1}$ surface structure have been removed. Clearly this image demonstrate that a 2.5 V bias voltage applied on the STM W-tip perturbs directly the atomic arrangement of the $\text{NbO}_{x \approx 1}$ surface structure.

3.3 Discussion

There are two possible physical explanations for these local modifications of $\text{NbO}_{x \approx 1}$ surface structure induced by a high bias voltage applied on a STM W-tip. The first one is the transfer of some tip atoms onto the sample surface assisted by electric field [16] - [18]. However, such transfers are weakly efficient in UHV [19] and only for one bias voltage polarity on an oxide as $\text{TiO}_2(110)$ [20]. Furthermore, the value of the applied tip voltage to transfer some metal atoms is higher than 2.5 V [21]. The second explanation is the transfer of some sample surface atoms onto the other electrode assisted by electric field. Also, this direct influence of a high electric field could perturb the atomic arrangement of $\text{NbO}_{x \approx 1}$ surface. A good illustration of this effect is presented in Fig. 5, where the $\text{NbO}_{x \approx 1}$ surface structure is partially destroyed by high bias tip voltage scanning. This may be attributed to the formation of oxygen vacancies on $\text{NbO}_{x \approx 1}$ surface [20].

In a first approximation, and neglecting the effect of the electric field enhancement at the STM tip apex, we can express the surface electric field E^m , associated to V_t^m , by

$E^m = V_t^m/d$. As d varies with tip and sample work functions and besides with I_t , it is difficult to evaluate it precisely. However, a reasonable estimated value is $5 \pm 2 \text{ \AA}$ [18]. This yields an electric field threshold at which modifications take place on $\text{NbO}_{x \approx 1}$ surface : $E^{mT} = 6000 \pm 1000 \text{ MV.m}^{-1}$, to compare with the maximum peak field $E_{pk} \approx 70 - 100 \text{ MV.m}^{-1}$ for the SCRF cavities. So, if the surface of these cavities is only covered with the niobium oxide $\text{NbO}_{x \approx 1}$, studied here, an electric field $E_{pk} \approx 70 - 100 \text{ MV.m}^{-1}$ would induce permanent degradations of this oxide when surface contaminants or defects yield a reasonable value of the electric field enhancement factor $\beta \approx 60 - 80$.

In summary, using a STM under UHV, we show that a $\text{NbO}_{x \approx 1}$ surface may suffer irreversible and permanent modifications above an electric field threshold $E^{mT} = 6000 \pm 1000 \text{ MV.m}^{-1}$. As a consequence for SCRF cavities, contaminants or defects yielding an electric field enhancement factors of about 70 could induce this kind of modifications.

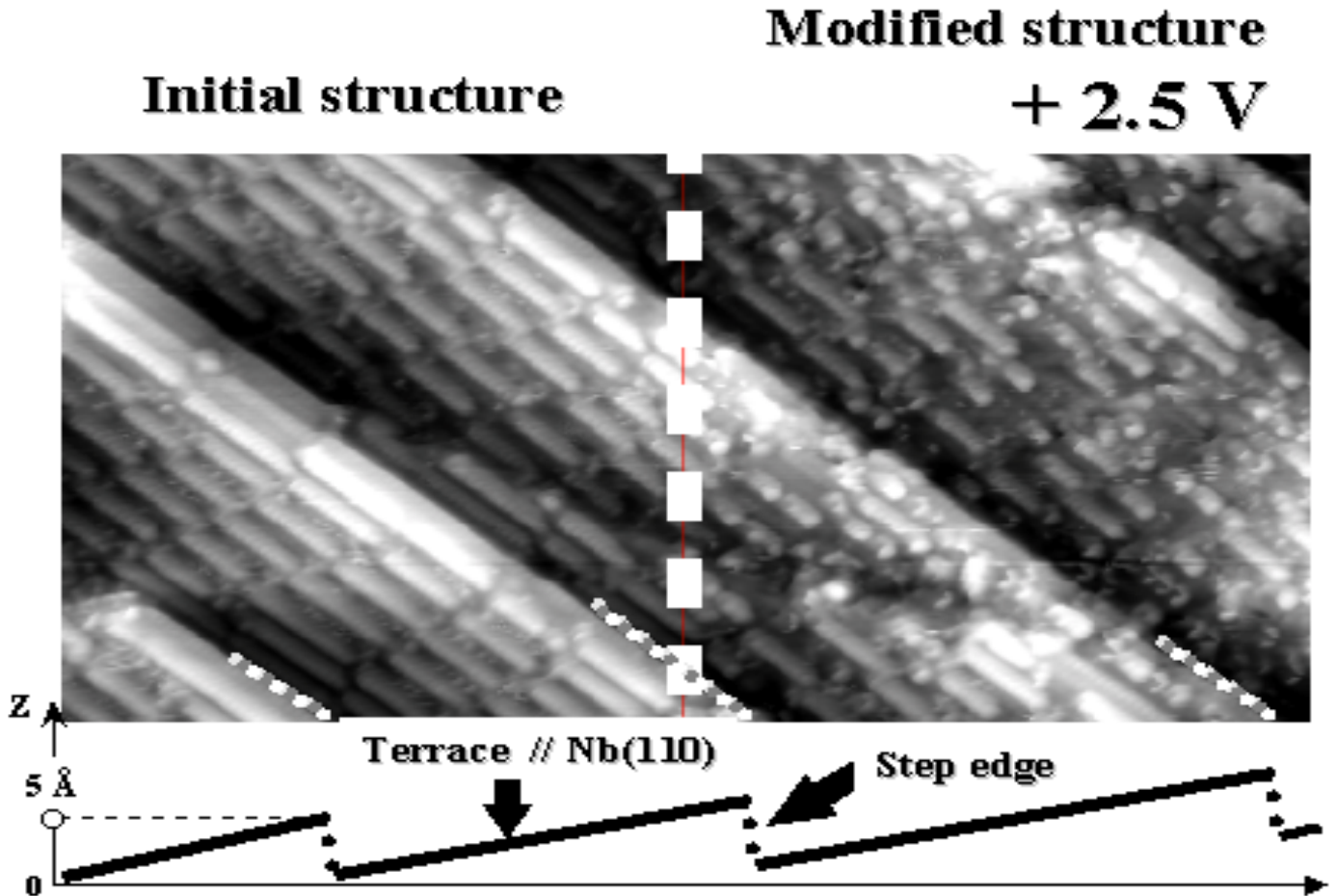


Figure 5: STM image (51 nm x 25 nm) of the modifications of the $\text{NbO}_{x \approx 1}$ stepped surface structure induced by a positive bias voltage near the threshold. On the left side, the “normal” area is taken as reference and on the right side, the “perturbed” area. Comparison of both sides of this image reveals that step edges are unperturbed. There are some perturbed sticks too. Finally, some zones without sticks and some white spots are observed.

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